DECLARATION

I, Yoshiyuki OHTSUKA of c/o 15-2, Hongo 1-chome, Bunkyo-ku, Tokyo 113-0033, Japan do solemnly and sincerely declare

1. that I am well acquainted with both the English and Japanese languages, and

2. that the attached document is a true and correct translation of the specification accompanying the application for a patent made in Japan filed on August 7, 2000 numbered P2000-237902.

And I make this declaration conscientiously believing the statements contained herein to be true in every particular.

Tokyo, Japan
Place

July 4, 2003
Date

(Signature of Translator)

TK0231-OP

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(ARTICLE)	Drawing 1
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[Title of the Document] Specification

[Title of the Invention] Precious Metal-Based Amorphous Alloy

[Claims for the Patent]

[Claim 1]

A precious metal-based amorphous alloy having a Pt-Cu-P based structure, wherein it comprises, in atomic %, $50 \leq Pt \leq 75\%$, $5 \leq Cu \leq 35\%$, and $15 \leq P \leq 25\%$.

[Claim 2]

A precious metal-based amorphous alloy having a Pt-Cu-P based structure comprising, in atomic %, $50 \leq Pt \leq 75\%$, $5 \leq Cu \leq 35\%$, $15 \leq P \leq 25\%$ obtained from solidifying the alloy in a molten state at a cooling rate of 10^{-1} to 10^{2}°C/sec.

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

The present invention relates to a precious metal-based amorphous alloy used as a material for accessories or medical devices. Specifically, the present invention relates to a precious metal-based amorphous alloy rich in platinum components and free of nickel which may have an influence on the human body.

[0002]

[Prior Art]

Precious metals such as gold and platinum have been used for medical devices such as dental instruments and catheters in addition to accessories such as rings, necklaces and pendants. Each of the materials used for these applications is required to have a higher hardness because the material needs to be prevented from scoring which is caused by the friction in use. A pure

precious metal, which is soft and vulnerable, is generally alloyed with a small amount of other metal elements when the precious metal is used as a material for the accessories and the medical devices. However, thus prepared precious metal alloys do not always have a fully satisfying property in terms of hardness.

[0003]

A crystal structure of an amorphous alloy which is also referred to as a super-cooled metal or a glass metal is different from that of a general metal material, and this amorphous alloy is a material having a random atomic arrangement throughout the super wide range. This structure provides some features that defects which would otherwise exist in its crystal structure (grain boundaries, twin crystals) can not be seen, so its physical characteristics such as strength show specific tendencies, and particularly its hardness becomes extremely high. This amorphous alloy is manufactured by super-quenching the liquid state alloy, so that the cooling rate in this case is required to be at an adequate level for inhibiting the production of crystal nuclei and their growth (a critical cooling rate) (for example, a critical cooling rate for a precious metal alloy is approximately 10^2 to 10^4°C/sec. and critical cooling rates for other alloys are approximately 10^5 to 10^6°C/sec.). Such a limitation on the cooling rate has so far resulted in a restriction of a size of the amorphous alloy which can be manufactured, that is, only some types of materials including foil-like, needle-like, and flake-like materials can be manufactured, so that it has been difficult to use these alloys industrially.

[0004]

However, with respect to an alloy metal having a predetermined composition, it has been recently found out that its material structure can be made into an amorphous state even at a relatively low cooling rate. This

results in the manufacture of a bulky (ingot-like) and thick amorphous alloy which is larger than the size of the hitherto known amorphous alloy such as a foil type material. As an alloy composition having such an ability of forming the amorphous state, various kinds of alloys have already been known. And applications of the amorphous alloys to the above described materials for accessories or medical devices, for example, are now under investigation.

[0005]

As an example of studying an amorphous alloy which contains a precious metal, for example, a Pd-Ni-P based amorphous alloy (in atomic %, Pd 40%, Ni 40%, and P 20%) is described in Japanese Patent Laid-Open No. 59-35417 as one of the transition metal-semi metal based amorphous alloys. Using the precious metal alloy having this composition, it has been demonstrated that the amorphous alloy about 5 mm in thickness can be manufactured even by the metal mold casting. In addition, Japanese Patent Laid-Open No. 9-195017 describes a Pt-Pd-Cu-Si based amorphous alloy (in atomic %, Pt+Pd: 65 to 80%, Cu: 0 to 15%, and Si: 10 to 20%) and discloses that the precious metal alloy having this composition can also be made into a bulk of 100 mm in length and 1 mm in diameter.

[0006]

[Problems to be Solved by the Invention]

However, these conventional amorphous alloys containing the precious metals are insufficient when considering their applications to the materials used for the accessories and the medical devices as described above. For example, the accessory is frequently desired to have an asset value as its aspect, and this asset value is commonly supposed to become greater in proportion to an amount of the precious metal contained in the accessory. Many of the conventional amorphous alloys contain less precious metals, so

that in this respect it can hardly be said that these amorphous alloys are suitable for the materials used for the accessories.

[0007]

In addition, many of the above described conventional precious metal-based amorphous alloys contain nickel as their components, but nickel is an element whose influence on the human body such as an metal allergy and carcinogenesis is worried. Therefore, it can be considered that these conventional amorphous alloys are not favorable to be used for substances which are in contact with the human skin continuously such as accessories and for substances which are in contact with the internal tissue of the human body of the human such as medical devices.

[0008]

The present invention has developed under the background as described above, and an object of the present invention is to provide an amorphous alloy which is rich in precious metals and is completely free of nickel provided that a bulk having an amorphous structure can be formed even when the alloy is solidified at a relatively low cooling rate.

[0009]

[Means for Solving the Problems]

The inventors have intensively made an effort to develop a precious metal-based amorphous alloy by which the above described problems can be solved. Specifically, the inventors have achieved the present invention as a result of selecting platinum as the precious metal which constitutes a principal component of the alloy, platinum being the most common material for accessories, to allow platinum to be contained at a level of 50% or more of the alloy, as well as selecting Cu and P as additional elements which have the ability to form the amorphous structure, and variously changing the

concentrations of theses elements to investigate the respective structures of the alloys.

[0010]

The present invention described in claim 1 is a precious metal-based amorphous alloy with a Pt-Cu-P based structure comprising 50% ≤ Pt ≤ 70% in atomic %, 5% ≤ Cu ≤ 35% by atom, and 15% ≤ P ≤ 25% in atomic %.

[0011]

An exact mechanism of forming the amorphous structure according to the present invention is not completely revealed, but it is supposed that copper and phosphorus both of which are additional elements have some effects of raising the crystallization temperature of the alloy and of expanding the temperature range of a super-cooled liquid (a difference between the crystallization temperature and the glass transition temperature) of the above described alloy, so that the ability of forming the amorphous structure is improved. In addition, the precious metal-based alloy with the Pt-Cu-P based structure according to the present invention can be made into amorphous states even when their cooling rates are relatively low by defining a range of copper concentration as 5% ≤ Cu ≤ 35% and a range of phosphorus concentration as 15% ≤ P ≤ 25% when a concentration of platinum is 50% or more and 75% or less.

[0012]

The precious metal-based amorphous alloy according to the present invention can contain up to 75% of platinum. Therefore, if the alloy is used for the accessories, an amount of the platinum contained therein can be expected to provide the accessories with the asset values. In addition, the precious metal-based amorphous alloy according to the present invention is completely free of nickel as is evident from its composition, so that the alloy is

supposed to have no effects on the human body which would otherwise cause metal allergy or carsinogenesis. In this respect, it also becomes possible to use the alloy for accessories and medical devices.

[0013]

The precious metal-based amorphous alloy according to the present invention can be made into a bulk material even when the alloy is cooled at a relatively low cooling rate. Therefore, an amorphous structure can be obtained even when the cooling rate is 10^2°C/sec. or less, but it is particularly preferable that the cooling rate is set at a 10^{-1} to 10^2°C/sec. Therefore, in claim 2, the precious metal-based amorphous alloy having a Pt-Cu-P based structure is defined to comprise, in atomic %, $50 \leq Pt \leq 75\%$, $5 \leq Cu \leq 35\%$, $15 \leq P \leq 25$ and is obtained by solidifying the alloy in a molten state at a cooling rate of 10^{-1} to 10^2°C/sec. The amorphous alloy according to claim 2 is a precious metal-based alloy which has been completely made into an amorphous state by setting the cooling rate during the solidification to be within an appropriate range. Setting the cooling rate to be within an appropriate range as described above, the amorphous alloy according to the present invention which has been completely made into its amorphous state has an extremely high hardness and is suitable for use as a material for accessories or medical devices.

[0014]

In addition, when the amorphous alloy of the present invention is made into a shape of its final product through casting, a surface of the alloy after being solidified becomes smooth, so that the solidified alloy can be marketed as a product as it is. On the other hand, if the amorphous alloy of the present invention needs to be processed, it is possible to cut the amorphous alloy, and also it is quite possible to subject the amorphous alloy to a composition

working although it has a high hardness. However, when the amorphous alloy according to a present invention needs to be subjected to a heavy working, it is preferable to heat the alloy to a temperature between its glass transition temperature and its crystallization temperature (a supercooled liquid temperature range) for performing the working. This is because, within the supercooled liquid temperature range, a viscosity of the amorphous alloy is abruptly reduced to cause a superplasticity phenomenon and so its workability increases.

[0015]

As a method for manufacturing the precious metal-based amorphous alloy according to the present invention, the alloy can be manufactured by mixing each metal and phosphorus within a range of the composition defined in claim 1 or 2 and by quenching the molten metal with this composition before solidifying the molten metal. When raw materials are mixed with and melted into each other, it is preferable to use powdery raw materials in order to promote the melting process. In this case, Cu which is in a pure metal state can be added, but Cu which is in a state of a copper-phosphide compound (Cu_3P and the like) can be added in order to make fine adjustments of the phosphorus concentration. Further, when these metals are allowed to be melted, it is preferable to add borax in order to prevent the alloy from oxidation. Although there is no particular problem about a method which is to be performed for quenching the alloy after the melting, a method for rapidly casting the alloy into a copper mold after the alloy is melted in a crucible being made of quartz for example is given as an example of the methods being capable of cooling the alloy at a cooling rate of 10^{-1} to 10^{2}°C/sec.

[0016]

[Embodiment]

Preferable embodiments according to the present invention will now be described below with reference to the drawings. In the present embodiment, a precious metal-based amorphous alloy was manufactured in the composition shown in Table 1, and a degree of amorphous state (hereinafter referred to as a vitrification degree) and a hardness of the alloy were measured to determine a composition range of the alloy having an amorphous structure.

[0017]

Various amorphous alloys were manufactured as follows. After platinum powder, powdery red phosphorus, and small bulky copper phosphide (Cu_3P) were weighed so that a total amount of these materials became 100 g in order to obtain a composition described in Table 1 and mixed with each other, 5 g of borax were further added to the mixture, then the mixture was placed in a one-side sealed-off silica tube having an inner diameter of 20 mm to heat it within an electric furnace in an atmosphere of argon and allow the materials to be melted. The melting temperature was determined to be at 1100°C, and after the materials were melted at this temperature, an argon gas was blown into the molten metals and bubbling was allowed to be generated for one minute in order to carry out stirring and degassing of the molten metals. Next, this molten metal was cast into a copper mold whose concave portion was in a ring shape (20 mm in outer diameter, 15 mm in inner diameter, and 50 mm in depth), and quenched and solidified to manufacture a ring shaped amorphous alloy.

[0018]

With respect to each of the amorphous alloys thus manufactured, after the alloy was cut into a predetermined dimension, a differential thermal analysis was conducted, then a vitrification degree of each alloy was investigated while measuring its glass transition temperature and

crystallization temperature. In this case, the differential thermal analysis was conducted by heating this alloy assuming that the weight of each amorphous alloy was constant within a range of 100 mg ± 10 mg, and the vitrification degree was determined from a height of an exothermic peak which may appear during the crystallization. For example, a specimen No. 7 (Pt: 60 at%, Cu: 20 at%, P: 20 at%) of FIG. 1 shows that its glass transition temperature is 238.5°C and its crystallization temperature is 286.0°C. In addition, after this determination of the vitrification degree was performed, a Vickers hardness of each alloy described above was measured. Both results of measuring the vitrification degree and the Vickers hardness with respect to each alloy described above are shown in Table 1.

[0019]

[Table 1]

Specimen No.	Element concentration (at%)			Degree of vitrification (Note)	Vickers hardness
	Pt	Cu	P		
1	50	35	15	○	450
2	50	30	20	◎	420
3	50	25	25	○	450
4	50	40	10	×	500
5	50	20	30	×	520
6	60	25	15	○	440
7	60	20	20	◎	410
8	60	15	25	○	450
9	60	30	10	×	510
10	60	10	30	×	500
11	70	15	15	○	430
12	70	10	20	◎	400
13	70	5	25	○	450
14	70	20	10	×	500
15	70	0	30	×	550
16	75	10	15	○	450
17	75	5	20	◎	420
18	75	0	25	×	490
19	75	15	10	×	500

◎: Completely vitrified

O: Almost vitrified

×: Crystallization

[0020]

As a result of this, an amorphous alloy having a composition according to this invention had a good vitrification degree and could be easily made into an amorphous structure, in addition, the alloy whose hardness is higher than a hardness of a platinum pure metal or a platinum alloy could be obtained. Every alloy was excellent in its gloss.

[0021]

Also, the specimen No. 7 had a density of 15.39 g/cc. Investigating the mechanical characteristics of this specimen No. 7 which was shaped into a ring shape having an outer diameter of 20.0 mm, an inner diameter of 16.0 mm, and a width of 3.0 mm, its compressive strength was 56 kg/cm^2. This alloy may have inscriptions thereon and its hardness and compressive strength are both higher than the platinum alloy, so that this alloy is considered to be suitable for the materials used for accessories.

[0022]

[Advantages of the Invention]

As described above, a precious metal-based amorphous alloy according to the present invention can be expected to have an asset value when the alloy is used for accessories because a concentration of the precious metal (platinum) contained in the alloy is high. In addition, since the precious metal-based amorphous alloy according to the present invention is completely free of nickel and has no bad influence on the human body, the alloy can also be expected to be used for the accessories for this reason. Similarly, the alloy is also applicable to medical devices.

[0023]

The precious metal-based amorphous alloy according to the present invention has a property of being able to be made into a bulk having an amorphous structure even when the alloy is solidified at a relatively low cooling rate in addition to other properties described above, so that it can be manufactured into scratch-proof accessories and medical devices by making full use of an inherent property of this amorphous alloy such as a high hardness.

[Brief Description of the Drawings]

[Figure 1]

Figure 1 shows a DSC curve of a sample No. 7 (Pt: 60 at%, Cu: 20 at%, P: 20 at%).

[Title of the Document] Abstract

[Abstract]

[Object]

An object of the present invention is to provide an amorphous alloy which is rich in precious metals and is completely free of nickel provided that a bulk having an amorphous structure can be formed even when the alloy is solidified at a relatively low cooling rate.

[Constitution]

The present invention is a precious metal-based amorphous alloy having a Pt-Cu-P based structure comprising, in atomic %, $50 \leq Pt \leq 75\%$, $5 \leq Cu \leq 35\%$, $15 \leq P \leq 25\%$. The alloy having this composition can be made into an amorphous structure by solidifying the alloy in a molten state at a cooling rate of 10^{-1} to 10^{2}°C/sec.

[Selected Drawing] None

FIG. 1